Reduction and Re-oxidation of Soils During and After Uranium Bioremediation; Implications for Long Term Uraninite Stability and Bioremediation Scheme Implementation

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(1) Introduction

This research focuses on the conditions and rates under which uranium will be remobilized via oxidation after it has been reduced and precipitated biologically, and what factors can contribute to increasing its long-term stability in groundwater after the injection of an electron donor has been discontinued.

(2) Research Hypotheses

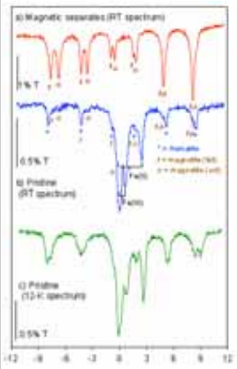
- Ferric (oxy)hydroxides, produced during the reoxidation of reduced soil, will "protect" a fraction of the reduced U(IV) from being reoxidized when the groundwater becomes more oxidizing after a bioremediation scheme is terminated.
- Short-term oxygen or nitrate pulses may regenerate bioavailable Fe(III), extending the operation of long-term schemes of uranium bioremediation under iron reducing conditions.
- FeS will buffer the reoxidation of U(IV) by preferentially reacting with oxygen when the groundwater becomes more oxidizing after a bioremediation scheme is terminated.
- Biomass can be a temporary redox buffer preventing U(IV) re-oxidation during the short term discontinuation of electron donor augmentation.

(3) Biostimulation / Re-oxidation Column Experimental Setup

- Four 15cm x 5cm columns packed with background sediment from Rifle, CO.
- Columns supplied 30mM bicarbonate buffer solution amended with vitamins and minerals.
- Flow rate of 0.2 ml/min
- Electron Acceptors:
  - Iron (soil)
  - Sulfate (9 µM)
  - Uranium (uranyl acetate) (20 µM)
- Electron Donor - Acetate (3 mM)
- Inoculated with *Geobacter metallireducens*

(4) Pristine Sediment Characterization

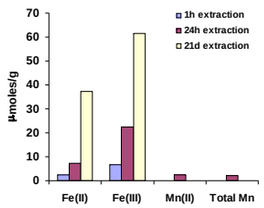
Mössbauer Analysis



- Powder X-ray diffraction detected quartz, muscovite, clinochlore, and calcite.
- Room temperature spectrum of the magnetic separates in the pristine sediment (figure a) indicates 0.02 – 0.05 wt % of the total sediment was "large particle" magnetite.
- Room temperature spectrum of the pristine sediment (figure b) indicates the following Fe phases:
  - magnetite (10-15 %)
  - hematite (5-10 %)
  - small particle (sp) Fe(III)-oxide (possibly goethite or ferrihydrite)
  - Fe due to muscovite and clinochlore
- ~30% of the total Fe was due to Fe(II) in clinochlore [Fe(II)-rich aluminosilicate] and/or muscovite [Fe-clay].
- ~40% of the total Fe was due to Fe(III) in muscovite and/or sp-Fe(III)-oxides.

Initial Fe and Mn in Sediment

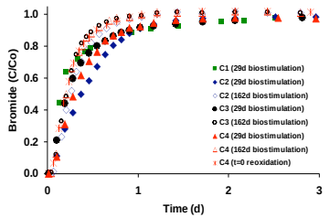
- Fe and Mn were quantified by 0.5 M HCl extraction (w/ and w/o hydoxylamine hydrochloride).
- Significant Fe(II) was present and Fe(II) concentrations increased with increasing extraction times).
- All of the measurable Mn was in the form of Mn(II).



(5) Timeline of Experiment

	Days of Biostimulation					Days of Re-oxidation	
	0	50	100	150	200	0	50
Column 1	==========>						
Column 2	==========>						
Column 3	==========>						
Column 4	==========	==========	==========	==========	==========		====>

(6) Bromide (Tracer) Breakthrough Curves

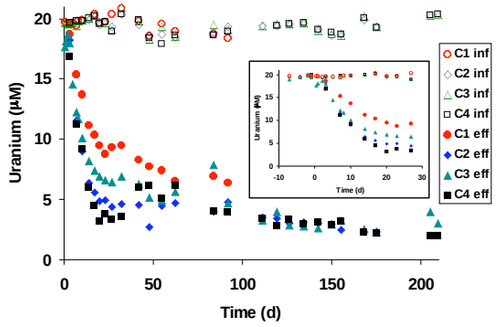


- Bromide breakthrough curves were performed after 29 days and 162 days of biostimulation and at the start of re-oxidation.

(7) Biostimulation Column Experiment

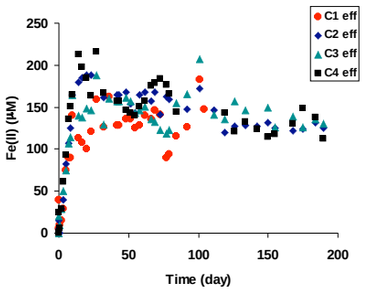
Four columns operated in parallel were inoculated with *Geobacter metallireducens* and reduced by continual addition of 3 mM acetate. One column was taken offline and destructively sampled after 104 days of biostimulation while another column was destructively sampled after 203 days of biostimulation (just before re-oxidation).

Uranium at Effluent



- Prior to acetate addition, no loss of uranium was measured in the column (insert).
- Acetate addition resulted in uranium removal from all four columns. The removal of 80-90% of the influent uranium concentration occurred after 200 days of acetate addition.

Fe(II) at Effluent

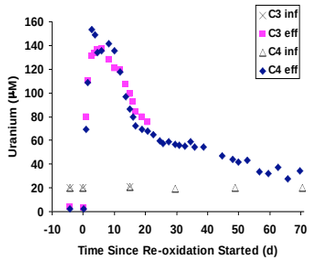


Fe(II) production occurred simultaneously with uranium precipitation and remained relatively constant throughout 200 days of biostimulation.

(8) Re-oxidation Column Experiment

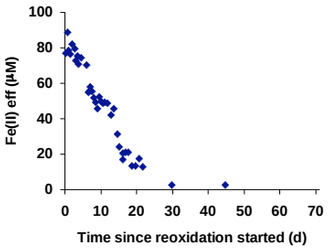
The two remaining columns were re-oxidized by stopping acetate addition and purging the influent media with 20% O_2. One column was taken offline and destructively sampled after 21 days of re-oxidation while the other column is still in operation (day 70 of re-oxidization). Oxygen has yet to be detected in the effluent (O_2 breakthrough has not occurred).

Uranium at Effluent



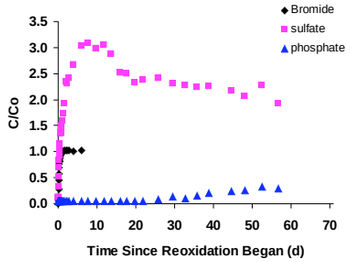
- Uranium was oxidized and re-dissolved upon addition of oxygen.
- 61% of the precipitated uranium was removed after only 21 days of re-oxidation.
- 99% re-dissolved after 70 days

Fe(II) at Effluent



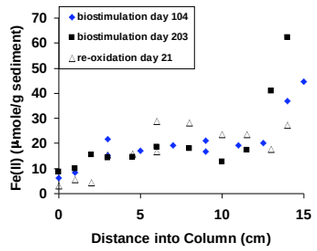
- Fe(II) continued to exit the column beyond 20 days (100 pore volumes) of oxygen addition.

Sulfate, Phosphate and Bromide at Effluent



- Initial sulfide oxidation follows a trend similar to uranium but exhibits longer trailing.
- About half of the sulfate removed during biostimulation was re-oxidized in the first 60 days.
- Phosphate (removed during biostimulation) was detected at the effluent after 30 days of re-oxidation (influent PO_4^{3-} conc. = 15 µM).

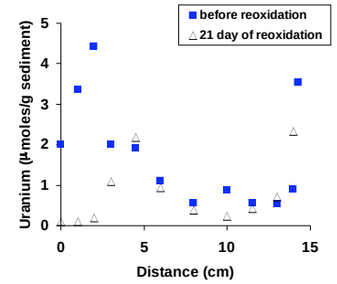
(9) Surface bound Fe(II)



- Surface-bound Fe(II) increased with distance into the column.
- Fe(II) concentrations remained relatively constant after day 104 of biostimulation.
- The amount of Fe(III) utilized during biostimulation (calculated from the Fe(II) produced that either sorbed to sediment or exited the column) was 26.6 and 36.6 µmol/g for the 104d and 203d experiments, respectively.
- Mossbauer analysis confirms a decrease in Fe(III) and an increase in biogenic Fe(II) during biostimulation.

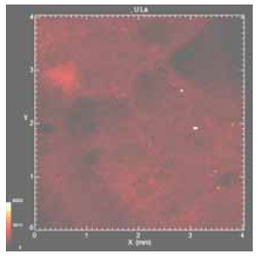
	Fe(II) Sorbed	Fe(II) Exported	Total Fe(II) Produced
Initial (t=0)	1.0 mmole		
104 d biostimulation	9.2 mmole	3.7 mmole	12.0 mmole
203 d biostimulation	7.9 mmole	7.3 mmole	14.2 mmole

(10) Surface-Bound Uranium

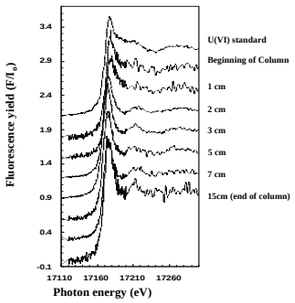


- Surface-bound uranium was extracted in 1M $NaHCO_3$ for 4 days and detected using ion chromatography.
- The majority of the uranium precipitation occurred at the beginning and end of the column during biostimulation.
- During short-term oxidation, uranium removal occurred at the beginning of the column

(11) Uranium Distribution and Speciation



- Sensitivity of X-ray absorption spectroscopy is low for detecting U in these sediments. Presence of high concentrations of Rb and Sr, which have fluorescence lines close to that of U, reduces the detection limits for U.
- Our X-ray microprobe analyses of U-reacted sediment samples indicate that U-distribution on sediment grains is uniform throughout the sediment column (see image on left). We also found that U concentration was significantly higher at the beginning and at the end of the columns.
- The U L3-edge XANES spectral analysis suggest that U is present in both U(VI) and U(IV) forms, with the reduced species present at a higher concentration beyond 5-7 cm into the column. Speciation did not change significantly beyond 5-7 cm as well.
- The uniform micron-scale distribution of U and its relatively high concentrations at the beginning and end of the columns indicate that the reduced forms of U may have formed nanoparticles and transported in this polymeric form.



(Synchrotron X-ray studies were conducted on Beamline X26A at the National Synchrotron Light Source.)

(12) Summary and Conclusions

- Initial sediment contained a significant amount of magnetite, hematite, muscovite, clinochlore and small particle Fe(III)-oxides (possibly goethite or ferrihydrite).
- Biostimulation resulted in 80-90% uranium removal from simulated groundwater.
- X-ray analysis indicate that a significant fraction of precipitated uranium was U(VI).
- Precipitated uranium was uniformly distributed on the solid phase at the micron scale (no hot spots).
- Virtually all of the uranium that had been retained during acetate biostimulation was flushed out of the system before oxygen breakthrough.

(13) Current/Future Work

- Column experiments examining nitrate re-oxidation.
- Acid volatile sulfide (AVS) analysis of sediments.
- Further analysis of precipitated uranium phases.
- Biomass characterization with time and space using phospholipid fatty acid (PLFA) analysis – Aaron Peacock (University of Tennessee).
- Biostimulation column experiments with significantly higher sulfate concentrations.
- In-Situ X-ray absorption spectroscopy.